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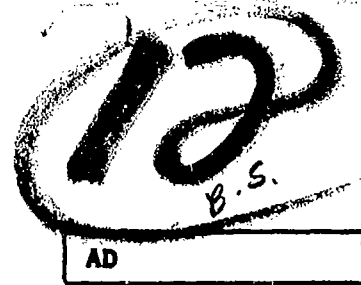
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CHARCOAL REGENERATION - PART II.
MODIFIED CARBON SURFACE ACTIVITY AND
REVERSIBILITY OF TNT ADSORPTION

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Chemical regeneration	Isotherms	carbon

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The TNT adsorption/solvent desorption cycling of activated carbon (FS300) has been studied as a function of various pretreatments. The preferential plugging of pores by the pretreatments did not enhance the regenerative property of the FS300. In conjunction with water adsorption/desorption isotherms, the characteristics of a carbon with an improved cycling property has been elucidated. The improved property is due to a shift to larger pore volume and a larger ratio of pore opening to pore body diameters. Chemical regeneration of activated carbon containing irreversibly adsorbed TNT has been shown to be unfeasible.

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INTRODUCTION

The use of granular activated carbon (GAC)[1] for the treatment of pink wastewaters at load and assembly Army Ammunition Plants has been established as an effective method of pollution abatement. However, its major drawback is the need to incinerate the spent carbon after the first breakthrough of RDX/TNT. The cost effectiveness of using GAC would be increased greatly by the repeated regeneration of the spent carbon in situ with solvent elution. In addition, the solvent can be recovered economically by vacuum distillation and the eluted TNT/RDX reused.

Accordingly, the regeneration of GAC by solvent elution was investigated and initially confined to TNT as the adsorbate (ref 1). It was concluded from this preliminary investigation that there is a loss of capacity of the carbon surface for TNT adsorption with each successive cycling by solvent (acetone) elution. This loss of capacity is due to the active nature of the carbon surface and/or the pore size distribution, leading to irreversible adsorption of TNT.

The TNT adsorbate molecules are attracted first to regions of the surface which have the highest energy. These regions are associated with various functional groups and high energy sites with surface carbon atoms having incomplete coordination numbers. A study of the relationship of energy site and/or pore size distributions representing the second phase of the investigation of the regeneration of carbon by solvent elution is the subject of this report.

EXPERIMENTAL

The activated carbon used in this study was FS300 obtained from Calgon Corporation, Pittsburg, PA. The carbon was ground to a 40/80 mesh, washed thoroughly, and dried. All pretreated samples were obtained from a master batch prepared in this way. Other GAC's used were FS400 from Calgon Corporation and Witco 337 (now designated as Grade 965) from Witco Corporation, New York, NY. These GAC's were also ground to a 40/80 mesh for comparison purposes.

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[1]The nomenclature "activated charcoal" is synonymous with activated carbon.

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Pretreatments

Gas Treatments

Methane, hydrogen, and argon were used to pretreat FS300. The carbon was placed in a quartz tube (50 cm by 1.6 cm) and the proper gas was allowed to flow through the tube, at a flow rate of 2-3 mL/min. After the air had been displaced, the tube was heated in a tube furnace to the previously calibrated temperature, and allowed to remain at this temperature for the requisite number of hours[2]. Cooling was carried out by allowing the gas to flow until room temperature was reached. The methane used was a 10% mixture of methane in 90% argon. Hydrogen and argon were high purity gases.

NO_2 and NO Treatments

The NO and NO_2 used were CP quality. The NO and NO_2 treated carbons were prepared by allowing the vapors to displace the air in stoppered flasks and allowed to remain in contact with the vapors at ambient temperature for the requisite time. Precautions were taken to absorb the excess vapors in caustic solution when preparing the samples.

Some preparations were water-washed to remove the unreacted NO_2 or NO. Others were washed with freon and/or acetone to remove the unreacted NO_2 or NO. All preparations were thoroughly dried in a vacuum desiccator prior to use.

Silanization

Five grams of FS300 (40/80) was heated overnight at 150°C. The carbon was placed in a one liter flask and covered with 75 mL of methyl cyclohexane. Ten mL of trimethylchlorosilane was added and the mixture refluxed under an air condenser for 5 hours. The solution was decanted, and 50 mL of n-propanol added to the carbon and refluxed for another hour. The alcohol was decanted and the carbon washed with n-propanol followed by oven drying at 110°C overnight.

Stearic Acid

Five grams of FS300 (40/80) was covered with 25 mL of 0.1% stearic acid in 95% ethanol in a beaker and allowed to stand over-night. The solution was decanted and the carbon allowed to air-dry.

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[2]See Table 1

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Water Adsorption Isotherms

Water adsorption isotherms were determined gravimetrically on a quartz spring balance (Worden Quartz Products, Inc) which had an absolute sensitivity of 7 micrograms per gram of sample. The water vapor pressures were measured with a 100 mm Barocol (Datametrics, Inc) capacitive differential manometer sensor and associated electronics enabling accurate readings to better than 10^{-3} mm.

Ultraviolet Analysis of Aqueous Solutions

A Beckman DU spectrophotometer equipped with one centimeter matched quartz cells was used for the analysis of aqueous solutions of TNT. A stock solution of TNT (100 ppm) was prepared by dissolving 100 mg of recrystallized TNT in one liter of distilled water. Aliquots of the stock solution were taken to prepare 1 to 10 ppm inclusively of standard TNT solutions. The absorbances of these standard solutions were measured on the spectrophotometer at 230 nm against a distilled water blank. The absorbances were plotted vs concentration giving a linear plot. Unknown solutions were diluted to a concentration in the range of 1 to 10 ppm. The absorbances were determined and their appropriate dilution factor applied to give the concentration.

Column Cycling (Adsorption-Desorption)

Critical column variables were determined for the column used in the column recycling part of this investigation. By taking into account various particle sizes and weights of carbon a design was developed which was suitable. This design allows a wide tolerance for the pressure head over the column.

A 34 x 106 cm glass column with 19/22 joints at both ends was plugged just above a joint at one end with glass wool. A "U" shaped siphon outlet was placed at this bottom end of the column and the top end fitted with a one liter funnel to hold stock TNT solution. The funnel was equipped with an overflow tube to allow excess solution to run back into the stock carboy (a 5-gallon polyethylene bottle). The solution was pumped to the funnel with a peristaltic pump timed to be activated 50% of the time, so as to maintain a constant head pressure ($\Delta v = 60$ mL).

Eight grams of GAC was accurately weighed into a 250 mL beaker and slurried with ca 100 mL water. The slurry was poured into the funnel and allowed to settle in the column with the aid of gentle tapping and a stream of water where necessary.

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The prepared column was clamped in the center of an automatic 20 position fraction collector (Buchler Instruments, Fort Lee, NJ). The fraction collector was equipped with an activator to periodically advance an adjustable glass funnel so as to collect the eluent in one liter polyethylene bottles.

On column cycling was carried out by monitoring the effluent for TNT concentration from the columns. The breakthrough point was standardized at an effluent concentration of 1 ppm. Loading the column with TNT was terminated as soon as sufficient data was generated to determine this point. The amount of TNT absorbed at 1 ppm effluent concentration was considered as the capacity of the carbon for comparison purposes. The specific adsorption of the column was calculated by dividing the total amount of TNT adsorbed by the weight of the carbon in the column.

After breakthrough, the column was desorbed by adding 100 mL increments of solvent, starting with 20% acetone/water in increments of 20% up to 100% acetone until one liter of eluent was collected. The column was then washed with distilled water until all acetone was washed out (several portions of 100 mL each). After water-washing, the column was ready for adsorption. The acetone extract was reserved for analysis.

The amount of TNT desorbed was determined by transferring the eluate to a one liter volumetric flask and diluting to the mark with acetone. A 10 mL aliquot was transferred to a 500 mL volumetric flask and diluted to the mark with water. A 10 mL aliquot was transferred to a 250 mL beaker, diluted to 100 mL with water, heated on a hot plate to evaporate ca 50 mL and insure the removal of the acetone. The remaining solution was transferred to a 100 mL volumetric flask, diluted to mark and the concentration determined by UV spectroscopy. The amount of TNT desorbed was calculated as follows:

$$\text{Amt. TNT, g} = \frac{1000}{10} \times \frac{500}{10} \times \frac{10}{100} \times \frac{1}{1000} = 0.5 \times C$$

where:

C = concentration determined in ppm.

Batch Cycling (Adsorption-Desorption)

One hundred mg of GAC was accurately weighed into a glass stoppered 1 L Erlenmeyer flask and 500 mL of a 140 ppm TNT solution added. This ratio of carbon to volume of stock TNT solution was always maintained to insure adsorption at the plateau region of the

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adsorption isotherm. The charged flask was placed on a wrist-action shaker and shaken for 24 hours to assure equilibrium. The amount adsorbed by the carbon was determined by withdrawing an aliquot of supernatant solution from the flask and determining the concentration of TNT by UV spectroscopy. The concentration, C_1, was subtracted from the initial concentration, C_0, of stock TNT solution and the specific adsorption calculated by the following:

$$\text{Specific adsorption} = \frac{C_0 - C_1}{2m}$$

where:

        m = weight of carbon, mg
        2 = correction factor for the volume of TNT solution used.

The TNT solution was carefully decanted from the carbon and rinsed once with a small quantity of water. Fifty mL of C.P. acetone was added to the flask and the stoppered flask was shaken for one hour. The acetone was decanted into a 250 mL volumetric flask. The process was repeated two more times with the washing being added to the volumetric flask. After dilution to the mark, a 5 mL aliquot was pipetted into a 250 mL beaker containing approximately 75 mL of water, and brought to a gentle boil on a hot plate to evaporate about 50 mL. This process expelled the acetone giving a residual aqueous solution of TNT which was diluted to volume (100 mL) in a volumetric flask. The concentration was determined by UV spectroscopy and the specific desorption calculated as follows:

$$\text{Specific desorption} = \frac{250}{5} \times \frac{100}{1000} \times \frac{C}{m} = 5\frac{C}{m}$$

where:

        m = weight of carbon (100 mg)
        C = concentration of TNT, ppm

The entire operation was repeated for the next cycle using the eluted carbon remaining in the flask.

Details of column cycling and batch cycling are presented in the Appendix.

Chemical Regeneration

The following procedures were carried out on TNT saturated FS300 carbon from which the reversibly adsorbed TNT had been

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extracted with acetone, and therefore, contained only irreversibly adsorbed TNT.

Alcoholic KOH: One gram of carbon was reacted at ambient temperature with 50 mL of 10% alcoholic KOH to produce a red color. The mixture was heated to 50°C, acidified with sulfuric acid and diluted to ca 200 mL with water.

Nitric Acid: Two gram of carbon was covered with concentrated nitric acid and heated gently for one hour. The mixture was allowed to cool and then washed thoroughly with water.

Ozonation: One gram of carbon was covered with water contained in a tube into which a diffuser was placed. Generated ozone was bubbled in for a period of two hours.

Oxalic Acid: One gram of carbon was covered with 100 mL of 5% oxalic acid and heated to boiling for 4 hours. The mixture was allowed to cool and stand overnight.

Reduction Procedures: One gram of carbon was reacted in a 1% sodium bicarbonate 1:1 ethanol-water solution with excess sodium dithionite.

One gram of carbon was mixed with ca 5 grams of zinc amalgam and covered with 5% HCl. After 15 minutes, 100 mL of water was added and the carbon separated from the zinc amalgam by flotation.

One gram portions of carbon were reacted with 1 g iron in 100 cm^3 of 30% HCl; 1 g tin in 100 mL 30% HCl, and 1 g NH_4 SH in 100 mL of 5% HCl.

A one gram sample of carbon was refluxed for one hour with 5 g $MgCl_2 \cdot 6H_2O$ and 2 cm^3 concentrated HCl.

In all cases after the reaction was terminated, the carbon was separated from the reaction mixture, washed thoroughly and dried at 110°C.

RESULTS AND DISCUSSION

TNT Cycling

Activated carbon shows chemical reactivity due to the presence at the surface of various chemical functionalities (ref 2). The microporous structure contains constrictions narrow enough to hinder

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the free passage of the TNT molecules and thereby renders some of the surface unavailable for its adsorption. Additionally, TNT may adsorb at constricted pore openings where the potential force field is sufficiently high to prevent desorption and where chemical reactivity may be promoted due to the long residence time of the adsorbate. Physically, adsorbed TNT is readily removed by acetone extraction; however, a portion of the TNT is irreversibly adsorbed leading to degradation of the adsorptive capacity. This capacity diminishes with successive cycling as the irreversibly adsorbed TNT accumulates. To obtain activated carbon which may be cycled without a significant loss of capacity, we must consider the chemical reactivity of the surface, the pore-volume distribution, and the surface area-pore volume relationship. That these factors are interrelated is evident in that reactivity leads to the closing of pores and loss of surface area.

The initial approach to this problem has been to pacify the surface by reacting the high energy sites with molecules which would then permit subsequently adsorbed TNT molecules to be easily desorbed. To evaluate the cycling characteristics of various GAC's, it was necessary to establish an experimental method which would permit adsorption/desorption cycling as rapidly as possible. For this purpose, we have designed a one point adsorption/desorption experiment; choosing the conditions so that the adsorption alway occurs at the plateau of the previously developed isotherm. Elution is maximized by allowing an excess of solvent (acetone) to contact the adsorbent-adsorbate complex for three periods of at least one hour each. This treatment was found to remove all the reversibly adsorbed TNT. (Soxhlet extraction did not remove significantly more TNT). Typically, carbons were batch cycled for six cycles to give a reasonable estimate of the behavior of the carbon insofar as degradation was concerned. A few carbons were cycled for up to 18 cycles (tables 8 and 9). The agreement between six cycles and many cycles is fairly close; hence, an extrapolation from 6 cycle results can be done with some confidence. By using this technique, a given pretreated sample could be evaluated in 1 to 2 weeks depending on the number of cycles required. Promising candidates were then selected for pilot columns study.

Granular activated carbons are manufactured in various mesh sizes and comparing these various carbons would involve differences due to diffusion. A 40/80 mesh size obtained by grinding was therefore utilized as the standard testing size so as to allow comparisons from one carbon to another[3]. This size allowed an

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[3]The periphery of a GAC particle may exhibit different properties from the central portion, therefore, any final testing must be carried out on the original particle size.

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increase in the loading and sharpened the breakthrough point of the columns. Testing in columns was caried out on a continuous adsorption basis to approach plant conditions as closely as possible. The specific adsorption of the columns, for the purpose of comparison, was calculated by dividing the amount of adsorbed TNT by the weight of the carbon used in the column, even though the TNT is not adsorbed uniformly over the length of the column.

Table 1 shows the effects of the various pretreatments upon the surface area of the FS300. It is evident that most of the pretreatments have lowered the surface area; a few treatments did not significantly change the area; hydrogen treatment at 1000°C increased the surface area by 10%. It is also shown that treatments with such reagents as NO_2 , NO, stearic acid, and methane at temperatures higher than 700°C have reacted with the carbon surface and closed off a portion of the micropore surface area.

Table 2 lists the values obtained from the linerization of the second order kinetic treatment of data from the cycling experiments (batch and column) on various 40/80 mesh untreated and pretreated activated carbons. A second order kinetic model is used because the data (the specific adsorption for consecutive cycles) fits this model, at least, to the extent of the cycling we have carried out.

The specific adsorption (zero intercept), C_o , at zero cycles and the slope of the equation were determined from a least squares analysis of the data. The correlation coefficient obtained is a measure of the mathematical validity of the devised equation, and the extent of deviation from the number one (1) is proportional to the degree of scatter of the data points. The slope of the line is related to the rate of degradation with cycling. The nature of the model is such that the slope is positive instead of an expected negative one. For a standard of comparison the virgin carbon was cycled in triplicate for the batch experiments. The initial capacities had a standard deviation of 0.01 and the slopes a standard deviation of 0.021.

As stated before, the experimental data follows the second order kinetic model (figs. 1 and 2). This relationship holds for both the batch experiments and the column experiments. The specific adsorption for the batch is at the isotherm plateau and the specific adsorption for the column is calculated at the 1 ppm breakthrough point.

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To evaluate the carbons, the areas under the degradation curves are integrated; this takes into account the rate of degradation and the capacity of the carbon. The areas may then be compared to FS300 as the standard. A significant increase in area indicates an improvement, and conversely, a decrease shows a poorer carbon.

The integrated linear plot gives the following equation:

$$A, \text{(Area)} = mn^2/2 + n/Co$$

Where:

$$A = \int y \, dn$$
$$y = 1/c$$

m = slope, n = cycle number
c = specific adsorption
Co = specific adsorption at n = o

Since the linear plot gives a value derived from a reciprocal relationship, for ease of comparison we have taken the reciprocal of A, so that a larger positive number shows an improvement over the standard.

Table 3 shows the areas calculated from the degradation curves of the various pretreated FS300's and two other commercially available carbons, namely FS400 and Witco 337. The significant difference at the 95% level for the batch experiments is 3×10^{-3}, and for the column experiments, 2×10^{-3}.

The GAC's which demonstrated some improvement in their cycling characteristics as evidenced by a higher area for the batch cycling experiments were the 1000°C hydrogen treated FS300, the FS400, and the Witco 337. The FS300 pretreated with methane, NO_2 and NO were chosen for column study for purposes of comparing their cycling characteristics.

The results in table 3 show a significantly higher area in the column cycling characteristics for the hydrogen treated carbon, the FS400, and the Witco 337. The other pretreated FS300 carbon, as previously indicated by the batch determinations show a lower area than the virgin FS300. The improvement for the hydrogen treated carbon in the batch experiments was borderline, yet the column experiment improvement was significantly greater. Since the hydrogen treatments were carried out at different times, it is possible that there may be slight differences due to variations in the preparations. This appears to be a common occurance with GAC, i.e., relatively poor reproducibility of adsorption properties. The FS400 and Witco 337 showed significantly higher areas under the curves and, therefore, improved cycling characteristics over the

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FS300.   The water adsorption-desorption isotherms for the carbons have given some insight into the reasons for these differences in cycling characteristics.

Water Adsorption/Desorption Isotherms

Water is unique as an adsorbate due to its unusual properties, which is explained by its intermolecular hydrogen bonding. The nature of water adsorption in the low pressure region of the isotherm up to a relative pressure of 0.4 is due to the presence of active sites from oxygen complexes on carbon. The water molecules hydrogen bond at these primary sites and act as secondary adsorption sites, and via hydrogen bonds, adsorb other water molecules. This results in complexes of water molecules forming in the pores (ref 3). As the pressure rises, the probability of adsorption increases due to the increase in the number of secondary adsorption centers. The steep rise in the adsorption isotherm curve in this relative pressure region is associated with the condensation in the pores which occurs as a function of related pressure and pore diameter according to the Kelvin Equation.

On the adsorption side of the hysteresis loop, the vapor pressure is in equilibrium with menisci in the body of the pores. On the desorption side, the vapor pressure is in equilibrium with menisci at the pore mouths. Thus, we can look at the hysteresis loop with the desorption leg desorbing in order of decreasing pore openings and the adsorption leg adsorbing in order of increasing pore diameters (ref 4).

Water adsorption/desorption isotherms shown in figures 3 through 7, were measured on 40/80 mesh carbon samples of FS300, FS400, Witco 337, and a series of FS300 pretreated samples. The water isotherms measured on all samples exhibited the characteristic S-shaped isotherm where the amount adsorbed at relative pressures below 0.4 was low due to surface hydrophobicity and where the adsorption increased rapidly in the relative pressure range of 0.4 to 0.8. Pronounced hysteresis was observed in the desorption leg for all isotherms. Carbons which were treated with NO_2 or NO showed an increased hydrophilicity, the isotherm (fig. 6) showing an early rise in the amount adsorbed. The general interpretation for these isotherms is that the surface is relatively hydrophobic, i.e., contain a low concentration of polar sites, and a high concentration of pores in the diameter range of 20 to 80Å , where the pore openings are smaller than the body of the pores. A detailed analysis of the results, however, indicated that all carbon samples showed differences in the degree of surface hydrophilicity and pore size distribution in the range investigated.

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The pore size analysis from the adsorption/desorption isotherms were carried out according to two procedures. One procedure, uses the adsorption/desorption isotherm for FS300 as the standard and compares the results obtained from the other samples with this standard. The results depicted in figures 8 and 9 and tabulated in table 4, show the change in pore size distribution relative to FS300. The absolute pore size distribution cannot be obtained from the water adsorption isotherms because a standard, i.e., a carbon sample known to contain no pores, does not exist for these carbon samples.

The results of the size distribution of the pore bodies relative to FS300 as shown in fig. 8 and in table 4 for FS400, Witco 337, and different pretreated samples of FS300, show that FS400 has a higher concentration of pores over the diameter range of 20 to 80A, which is the reason for the higher surface area of this sample. The Witco 337 charcoal shows a lower concentration of pores below 50A, and a much higher concentration above 50A. Both the methane and hydrogen high temperature treatment of FS300 lead to decreases in the pore size distribution between 20 and 80A. In the case of the hydrogen treatment, where the surface area has been increased, it must be assumed that this treatment shifts the pore size distribution to higher diameters (refs 5,6). Both the NO and NO_2 treatment of FS300 leads to an increase in pore diameter below 40 and 50A, respectively, and a decrease in higher diameter pores. Figure 9 and table 4, show the results of the analysis of size distribution for the pore openings relative to FS300. The results are similar to the changes shown for the pore bodies in that the Witco 337, and the methane and hydrogen treated FS300 all show initial decreases in the pore size distribution. The results are different, however, in that the decrease is over a much narrower range for Witco 337 and FS300/H_2/1000°C. In the second method, the pore size distribution is calculated from the hysteresis loop in the water adsorption-desorption isotherms (figs. 3 through 7). The results of this analysis, demonstrated in figures 10 and 11, show the pore size distribution of the pore opening relative to that of the body of the pore where the pore opening is smaller.

The results show that the hydrogen treated FS300 and Witco 337 have the highest concentration of pore size openings in the range of 30A to 80A with the Witco 337 being higher after extrapolating the experimental results. The FS300 and FS400 all showed similar pore concentration in this range. The NO and NO_2 treated FS300 both showed a decrease in the concentration of pore size openings in this range.

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The following conclusions can be drawn from this analysis. The FS300 and FS400 have pores which are similar in shape. The FS400, however, has a higher concentration of mesopores[4]. The Witco has a lower concentration of pores below 50Å and a much higher concentration of pores above 50Å, leading to a significantly higher surface area. The pores in the Witco sample also exhibit a high ratio of pore opening diameter to pore body diameter as compared to FS300 and FS400, in the range of 35Å to 60Å, but with a higher ratio below 35Å. However, the absolute diameter of the pore opening diameter increases above 35Å as compared to all the carbons investigated. The NO_2 and NO pretreatments of FS300 have the common effect of closing the pores with small openings and decreasing the size of larger pores, thus, decreasing the specific surface area. The methane pretreatment on FS300 has the effect of closing pores over a wider pore size range, but to a smaller extent than NO_2 and NO. Hydrogen pretreatment of FS300 has the effect of increasing the dimensions of the pores in the range of 30 to 60Å. The pore openings are especially affected in that they are decreased below 45Å and increased above this value with a subsequent increase in surface area.

Desorption

As pointed out in the previous report (ref 1), there is always some residual TNT remaining on the carbon due to chemisorption and/or very strong physical adsorption. Diffusion problems are also implicit in this connection as the time to desorb using acetone is much less than the time of adsorption. Table 5 shows the typical data derived from cycling a column of 40/80 mesh FS300. The first cycle desorption removes the least amount of TNT, subsequent desorptions remove significantly more. Although the analytical procedure has a relatively large error, it can be seen that each cycle leaves behind some irreversibly adsorbed TNT.

The data in table 6 under incremental desorption (for one desorption cycle) shows that most of the TNT is removed with the first few hundred mL of acetone, and that further exposure to solvent removes only minuscule amounts.

Chemical Regeneration

Most of the TNT adsorbed on activated carbon is easily desorbed with acetone. The residual is chemisorbed or held by very strong physical forces. Other solvents such as dimethyl formamide,

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[4]Mesopores have a width of from 20-500 .

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dimethylsulfoxide, benzene, and triethanolamine at temperatures up to 80°C were not effective in removing any more TNT, and were difficult to remove from the carbon. An investigation was carried out to determine if chemical reactions could solubilize this chemisorbed portion. As shown in table 7, chemical treatment of the carbon resulted in varying degrees of surface area loss. Treatment with alcoholic KOH, high temperature reaction with magnesium chloride hexahydrate, hydrochloric acid, zinc, nitric acid, oxalic acid, and ozonation all proved destructive to the surface area. As these methods would not be practical on a large scale, both for safety and economic reasons, further investigation of this phase was dropped. Previous attempts to chemically regenerate carbon have not been successful (ref 7).

CONCLUSIONS

The use of chemical regeneration is not feasible for the reactivation of GAC as it damages the pore structure, tends to be costly, and generates harmful by-products for disposal.

Due to the heterogeneous nature of the activated carbon surface, there is an inevitable loss of TNT adsorptive capacity after each successive adsorption/solvent desportion cycle. The standard carbon, FS300 as shown previously, has one third of its surface area unavailable to TNT adsorption. This fact, plus the loss of surface area due to irreversible adsorption at the high energy sites of the pore openings, accounts for its poor TNT cycling characteristics.

The TNT adsorption/desorption cycling behavior of the various pretreated and other carbons were compared to the standard carbon, FS300, by integrating the areas under the linear degradation curves, which were derived from a second order kinetic model. The integrated areas depend upon the rate of degradation (slope) and the specific capacity of the carbon for the TNT (y intercept). The highest areas will have high intercepts and a small slope. By means of water adsorption/desorption isotherms it was found that pretreated carbons which had lower integrated areas and hence, poorer TNT cycling capacity than the standard FS300, showed a decrease in the concentration of higher diameter pores. Conversely, the other carbons with higher integrated areas and hence, better TNT cycling capacity than the standard FS300 showed pore size distributions that had an increased concentration of pore diameters in the higher range, i.e., from 50Å to 100Å, and a higher ratio of pore opening diameter to pore body diameter.

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The observations summarized above, have lead to an understanding of the requirements for a GAC which would be more suitable for the adsorption/solvent regeneration cycling of TNT. This improved GAC should have an increased pore concentration in the pore diameter range of from 50Å to 100Å, with a high ratio of pore opening diameter to pore body diameter. The larger pore openings would tend to minimize the blockage of pores by the irreversible adsorption of TNT at the high energy sites of the pore openings. The present carbon, high in micropore concentration, should therefore, be replaced by a commercially available carbon high in the lower diameter size range of mesopores. To this end, carbons should be screened by TNT adsorption/desorption cycling and pore size distribution determinations for optimum regenerative behavior.

REFERENCES

1. T.C. Castorina, J. Haberman, and J. Sharma, "Charcoal Regeneration, Part I; Mechanism of TNT Adsorption," Technical Report ARLCD-TR-77065, ARRADCOM, Dover, NJ, Nov 1977.

2. J.B. Donnet, Carbon, $\underline{6}$, 161 (1963).

3. M.M. Dubinin, Chemistry and Physics of Carbon, Vol 2, Marcel Dekker, NY, 1966.

4. A.J. Juhola and E.O. Wiig, Amer. Chem. Soc. $\underline{71}$, 2069 (1949).

5. J. Holmes and P.H. Emmet, J. Phys. Colloid Chem. $\underline{51}$, 1276 (1947).

6. H.L. McDermot and J.C. Arnell, J. Phys. Chem. $\underline{58}$, 494, (1954).

7. Summary Report, "The Advanced Waste Treatment Research Program," US Dept of Health, Education and Welfare, April 1965.

Table 1. Surface areas of virgin and pretreated carbons.

Treatment	Surface area, m^2/g
FS300 (virgin)	1026
TNT-sat/soxh-ext	578
CH_4/4 hr/600°C	1044
CH_4/4 hr/650°C	976
CH_4/3 hr/700°C	1044
CH_4/5 hr/700°C	1065
CH_4/4 hr/750°C	649
Ar/4 hr/1000°C	1049
H_2/4 hr/1000°C	1157
NO_2/72 hr/H_2O	694
NO_2/72 hr/freon	696
NO_2/72 hr	777
NO_2/72 hr/freon/acetone	537
NO_2/18 hr	650
NO_2/4 hr	693
NO_2/14 hr/freon	642
NO/72 hr/H_2O	842
NO/4 hr/freon	811
NO/4 hr/ H_2O	805
NO/4 hr/freon/acetone	732
Silanized	959
Stearic acid	741
Witco	1311
FS400	1119

Table 2. Rates of degradation of pretreated carbons .

	Batch		
Treatment	Slope	C_0	Correlation coefficient
FS300 (virgin)	0.128	0.49	0.92
TNT-sat/soxh ext	0.294	0.42	0.88
CH_4/4 hr/600°C	0.169	0.41	0.90
CH_4/4 hr/650°C	0.184	0.45	0.96
CH_4/3 hr/700°C	0.080	0.44	0.91
CH_4/5 hr/700°C	0.120	0.44	0.86
CH_4/4 hr/750°C	0.096	0.28	0.69
Ar/4 hr/1000°C	0.141	0.44	0.89
H_2/4 hr/1000°C	0.135	0.52	0.95
NO_2/72 hr/H_2O	0.150	0.35	0.86
NO_2/72 hr/freon	0.124	0.33	0.94
NO_2/72 hr	0.304	0.38	0.99
NO_2/72 hr/freon/acetone	0.199	0.29	0.79
NO_2/18 hr	0.116	0.32	0.68
NO_2/4 hr	0.205	0.35	0.97
NO_2/4 hr/freon	0.139	0.32	0.82
NO/72 hr/H_2O	0.161	0.38	0.87
NO/4 hr/freon	0.207	0.40	0.96
NO/4 hr/H_2O	0.060	0.44	0.87
NO/4 hr/freon/acetone	0.083	0.33	0.67
Silanized	0.231	0.52	0.91
Stearic acid	0.234	0.47	0.96
Witco 337	0.063	0.63	0.97
FS400	0.041	0.55	0.75

	Column		
FS300 (virgin)	0.250	0.50	0.94
CH_4/4 hr/700°C	0.353	0.48	0.93
H_2/4 hr/1000°C	0.335	0.76	0.98
NO_2/72 hr	0.468	0.33	0.93
NO/4 hr/H_2O	0.289	0.40	0.78
Witco	0.183	0.63	0.98
FS400	0.232	0.57	0.89

All carbons were FS300, 40/80 mesh, unless otherwise listed.

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Table 3. Integrated areas under degradation curves .

| | Area $\times 10^{-3}$ | |
Treatment	Batch	Column
FS300, virgin	69	61
CH_4/5 hr/700°C	63	53
H_2/4 hr/1000°C	72	72
NO_2/72 hr	54	55
NO/4 hr./H_2O	53	50
FS400	86	68
Witco 337	94	78
TNT sat'd/extracted	51	-
CH_4/4 hr/600°C	56	-
CH_4/4 hr/650°C	60	-
CH_4/3 hr/700°C	66	-
CH_4/4 hr/750°C	43	-
Ar/4 hr/1000°C	62	-
NO_2/72 hr/H O	50	-
NO_2/72 hr/freon	49	-
NO_2/72 hr/acetone	41	-
NO_2/18 hr.	48	-
NO_2/4 hr	48	-
NO_2/4 hr/freon	47	-
NO/72 hr/H_2O	34	-
NO/4 hr/freon	53	-
NO/4 hr/freon/acetone	51	-
Silanized	64	-
Stearic acid	59	-
Significant diff. at 95% level	3	2

All carbons were FS300, 40/80 mesh, unless
otherwise listed.

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Table 4. Change in porosity of pretreated and other activated carbons compared to 40/80 FS300.

Sample	Area under degradation curves x10^{-3}		Porosity		
			<50A		>50A
	Batch	Column	Body	Opening	Opening
Witco 337	94	78	-30	-60	+130
B$_2$A 4 hr/1000°C	72	72	-85	-140	+10
FS400	86	68	+60	+60	+30
FS300	69	61	0	0	0
NO$_2$/72 hr	54	55	-100	+130	-25
CH$_4$/5 hr/ 700°C	63	53	-60	-120	-30
NO/4 hr/H$_2$O	53	50	-60	+80	-75

Table 5. Column adsorption/desorption cycling.

Cycle number	Breakthrough, Specific ads. at 1 ppm	Total specific adsorption	Specific desorption	Percent desorption
1	0.48	0.53	0.39	73.6
2	0.39	0.42	0.36	85.7
3	0.36	0.39	0.32	82.0
4	0.34	0.38	0.34	89.5
5	0.32	0.38	0.30	78.9
6	0.29	0.34	0.33	97.1
7	0.30	0.36	0.33	91.7

Table 6. Incremental column desorption for one cycle.

Increment number	Volume, mL	Amount desorbed/g
1	300	1.750
2	100	0.165
3	100	0.006
4	200	0.010
5	100	0.014
6	100	0.009
7	100	0.006
Total	1000	1.960

Amount adsorbed was 2.52g - 77.8% desorbed.

Table 7. Effect of chemical regeneration
on surface area of FS300.

Treatment	Surface area, m^2/g
None*	945
Sulfuric acid	848
Reduction	318
Reduction	655
Oxalic acid	714
Ozone	723
Nitric acid	469

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*40/80 mesh FS300 was saturated with TNT and
then soxhlet extracted with acetone.

Table 8.   Batch cycling of 40/80 mesh FS300/Argon/4 hrs/1000°C.

Cycle number	Specific adsorption
1	0.41
2	0.42
3	0.34
4	0.36
5	0.34
6	0.32
7	0.27
8	0.27
9	0.27
10	0.27
11	0.26
12	0.23
13	0.24
14	0.23
15	0.22
16	0.15
17	0.15
18	0.15

$\frac{1}{C} = 0.235n + 1.806$

corr. coeff. = .917

Table 9. Batch cycling of 40/80 mesh FS300/CH_4/600°C/4 hr.

Cycle number	Specific adsorption
1	0.38
2	0.31
3	0.34
4	0.35
5	0.31
6	0.32
7	0.27
8	0.26
9	0.23
10	0.24

$\frac{1}{C}$ = 0.174n+2.453   corr coeff. = .909
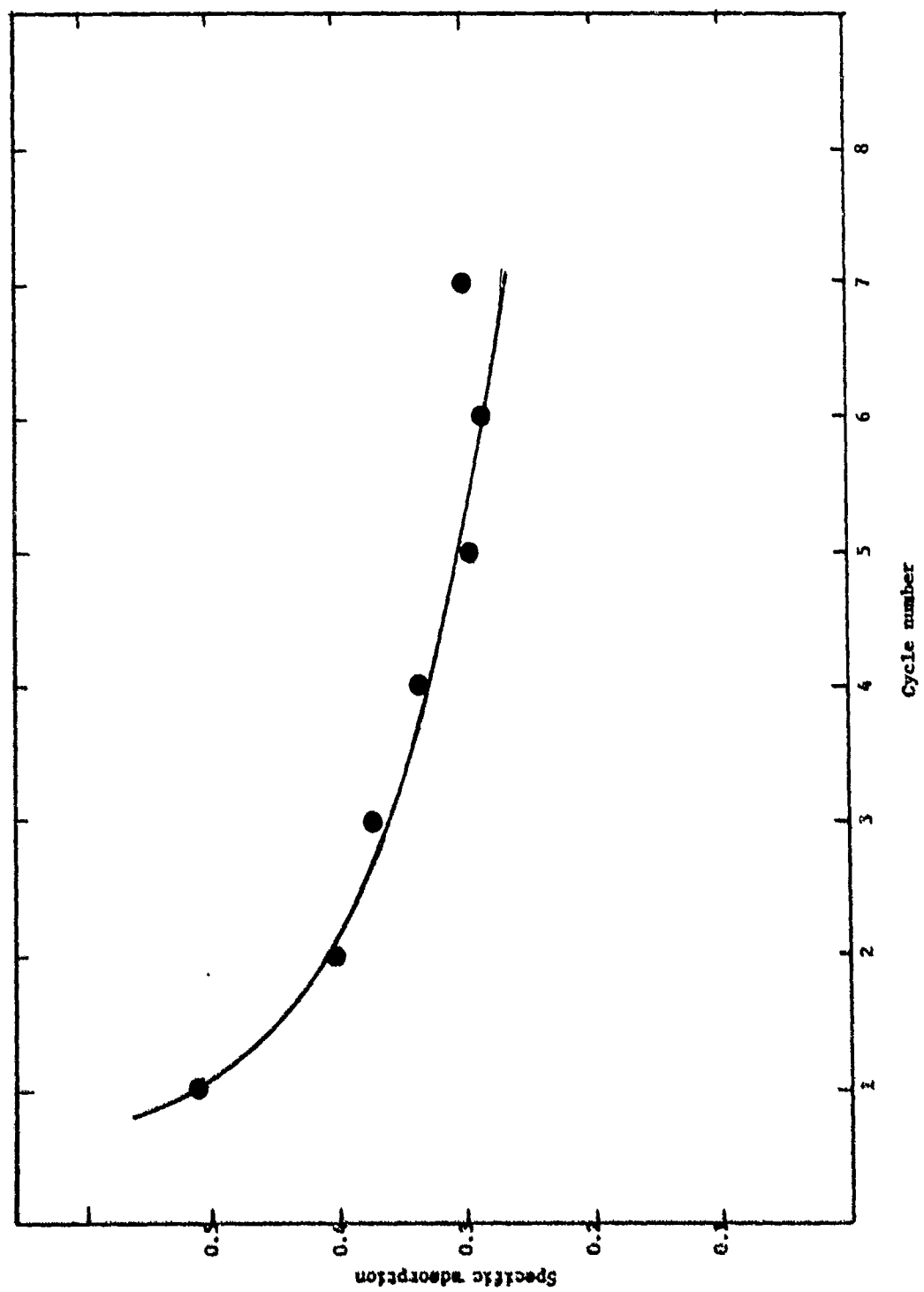
Figure 1. Specific adsorption deactivation as a function of adsorption/desorption cycling.

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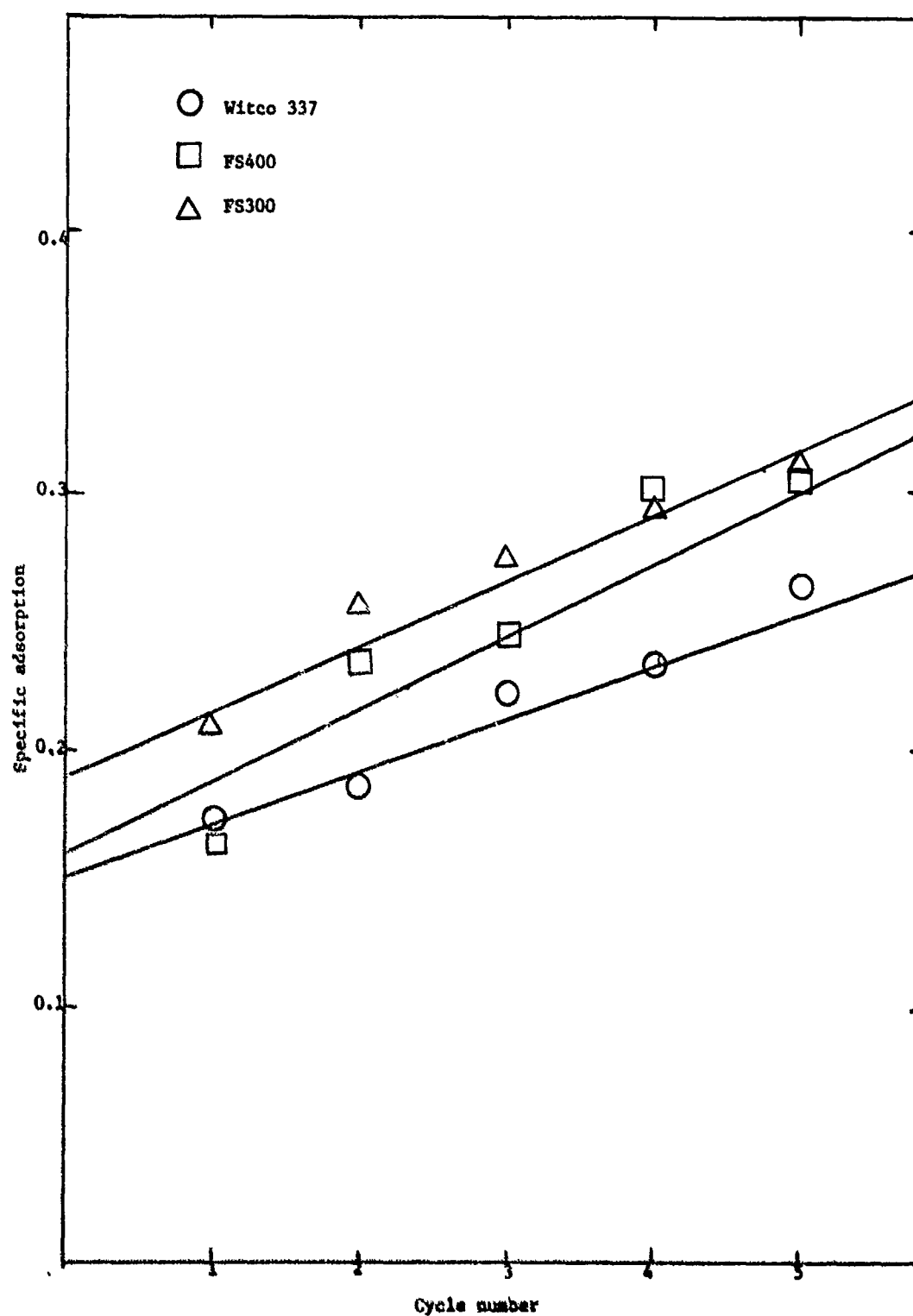
Figure 2. Linear plots of specific adsorption deactivation as a function of adsorption/desorption cycling according to a second order kinetic model.

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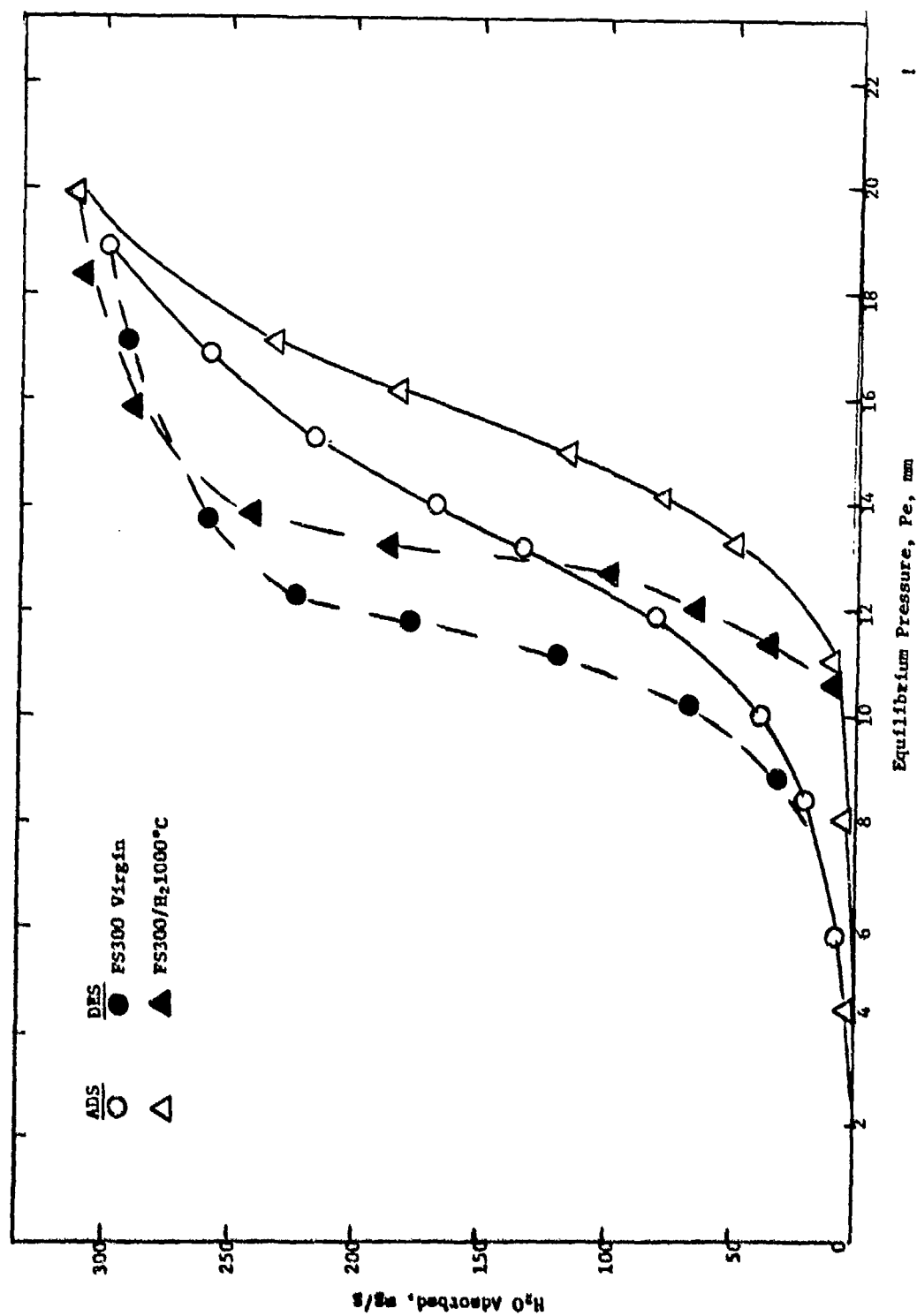
Figure 3. Water adsorption/desorption on 40/80 FS300 and hydrogen treated 40/80 FS300 at 1000°C for 4 hr

25
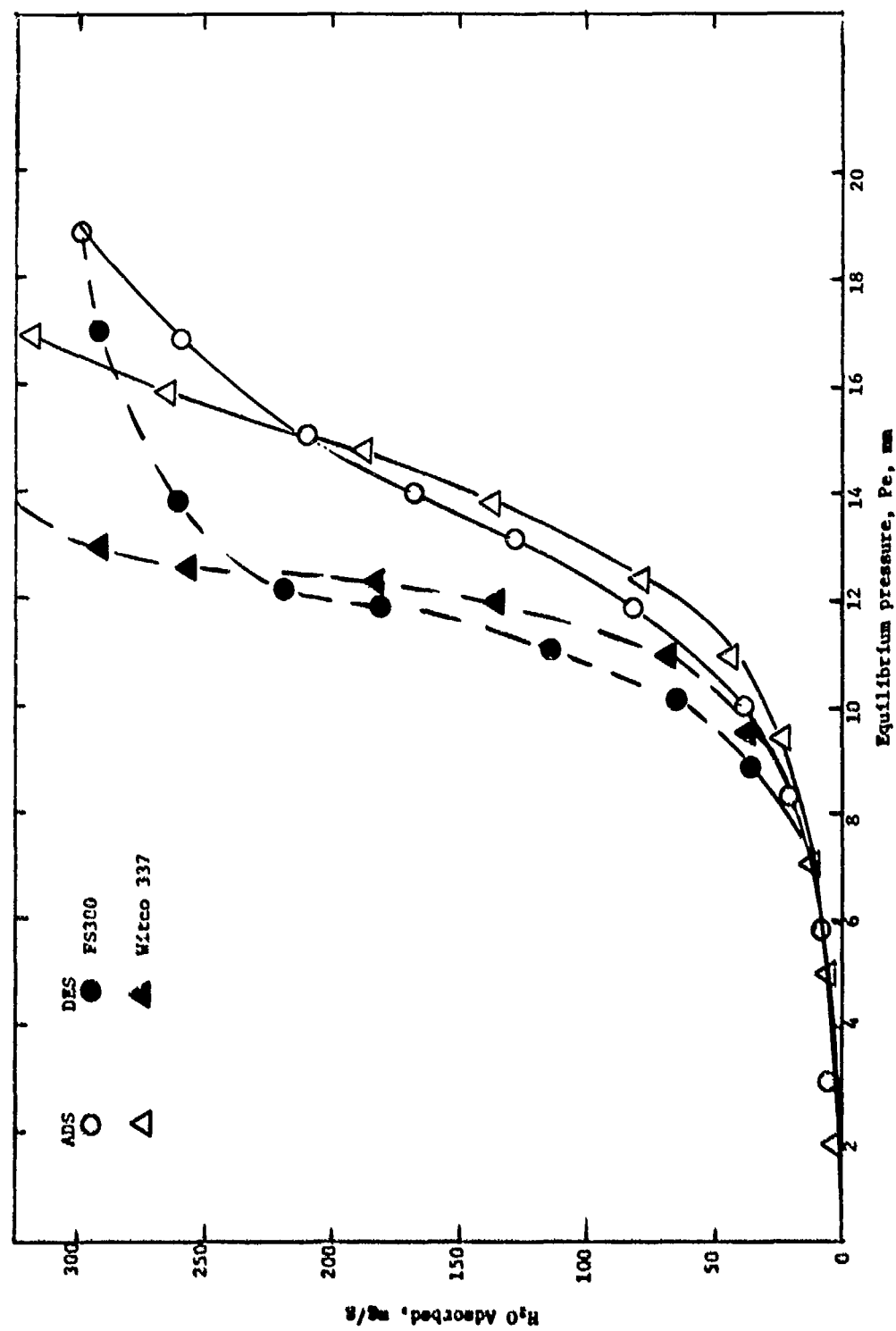
Figure 4. Water adsorption/desorption on 40/80 FS300 and 40/80 Witco 337.

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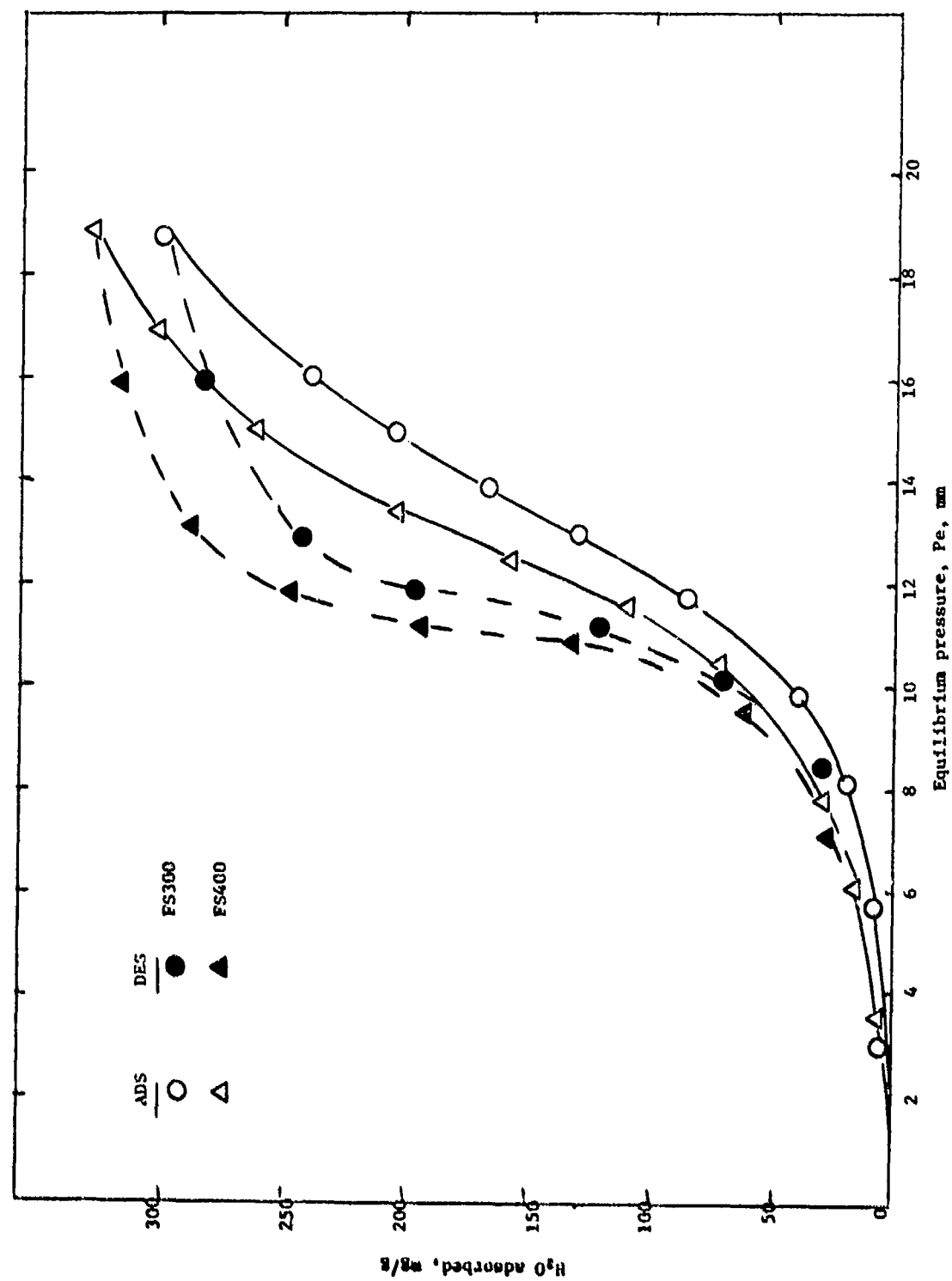
Figure 5. Water adsorption/desorption on 40/80 FS300 and 40/80 FS400.
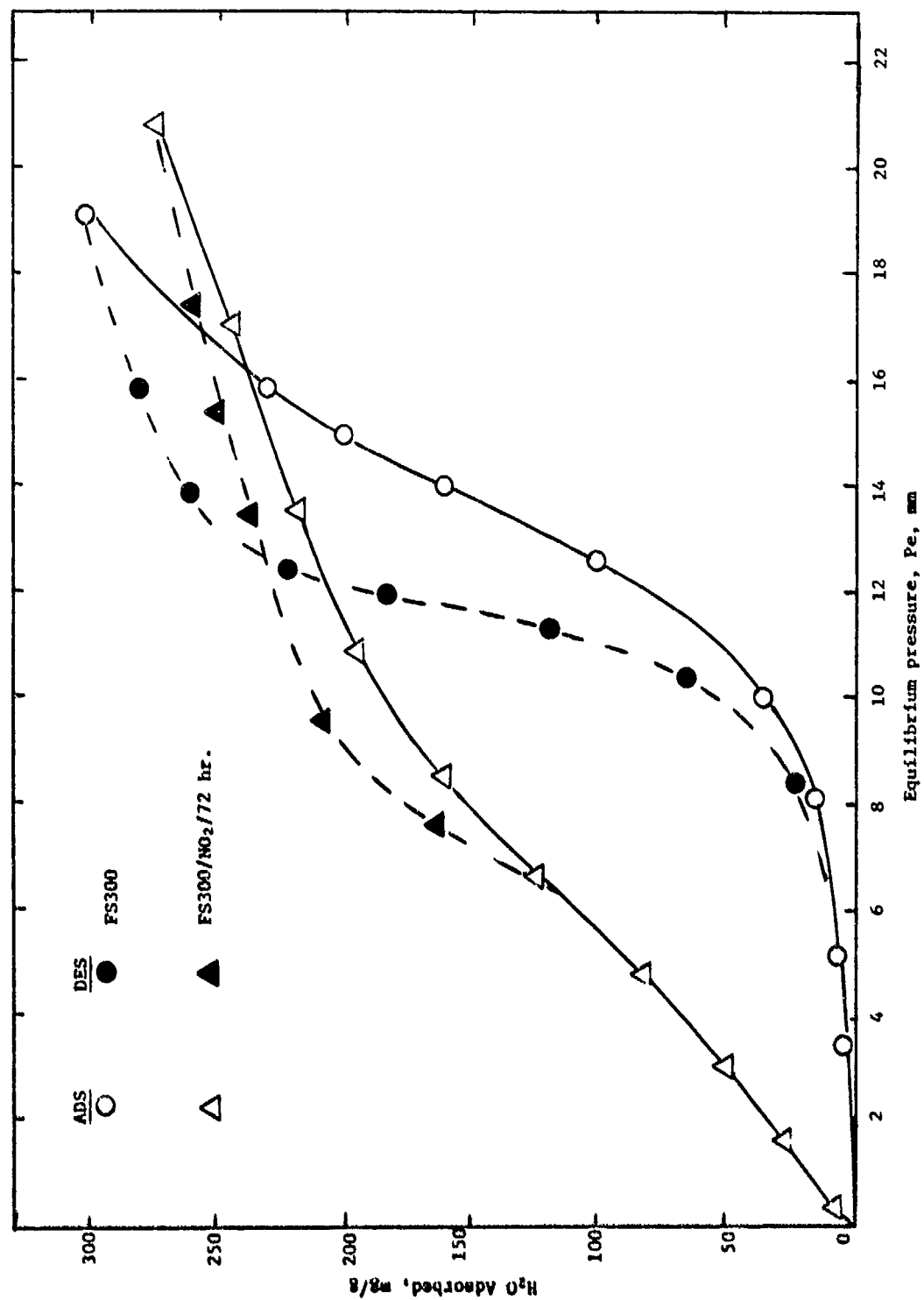
Figure 6. Water adsorption/desorption on 40/80 FS300 and 40/80 FS300 treated with NO_2 for 72 hr.
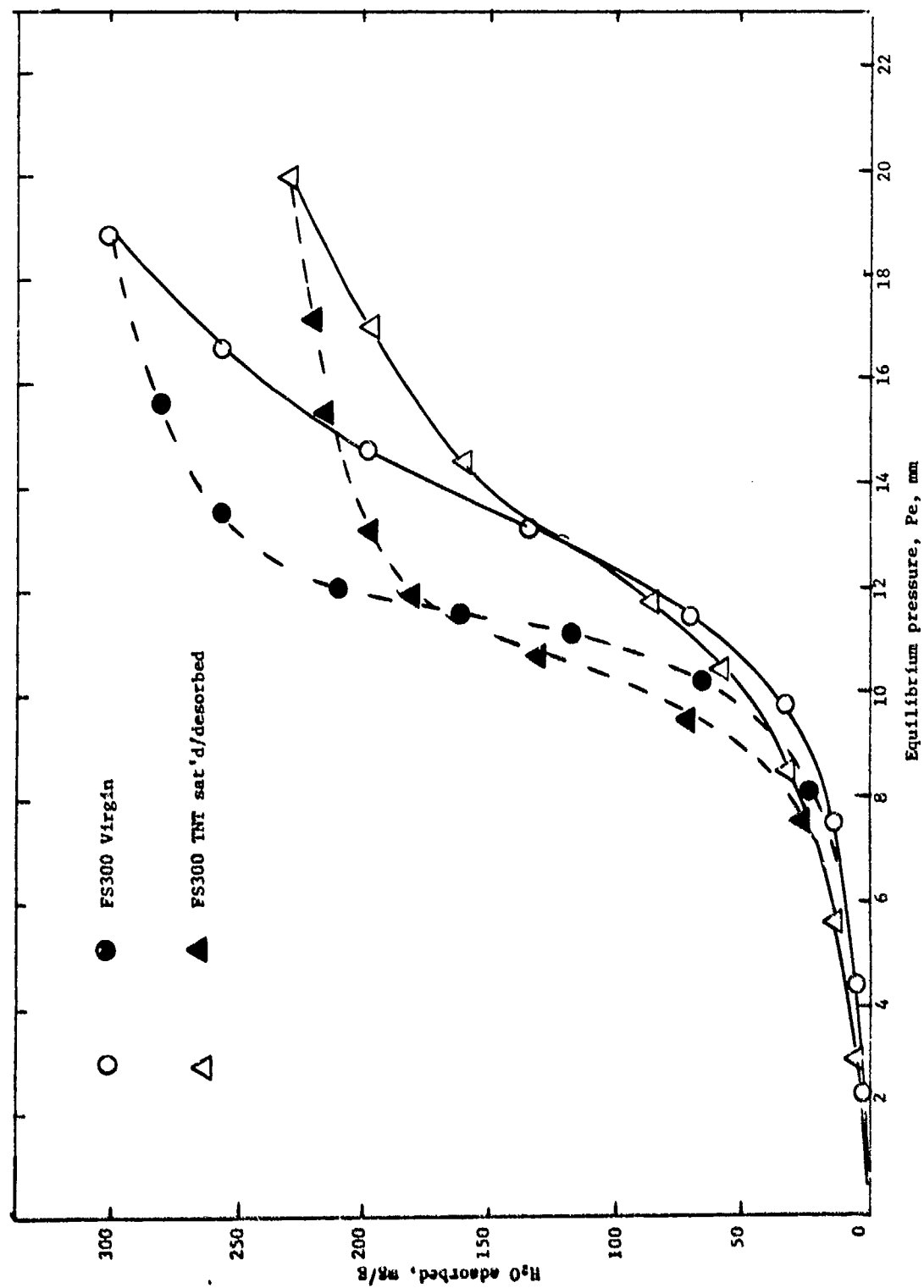
Figure 7. Water adsorption/desorption on 40/80 FS300 and TNT saturated-desorbed 40/80 FS300.
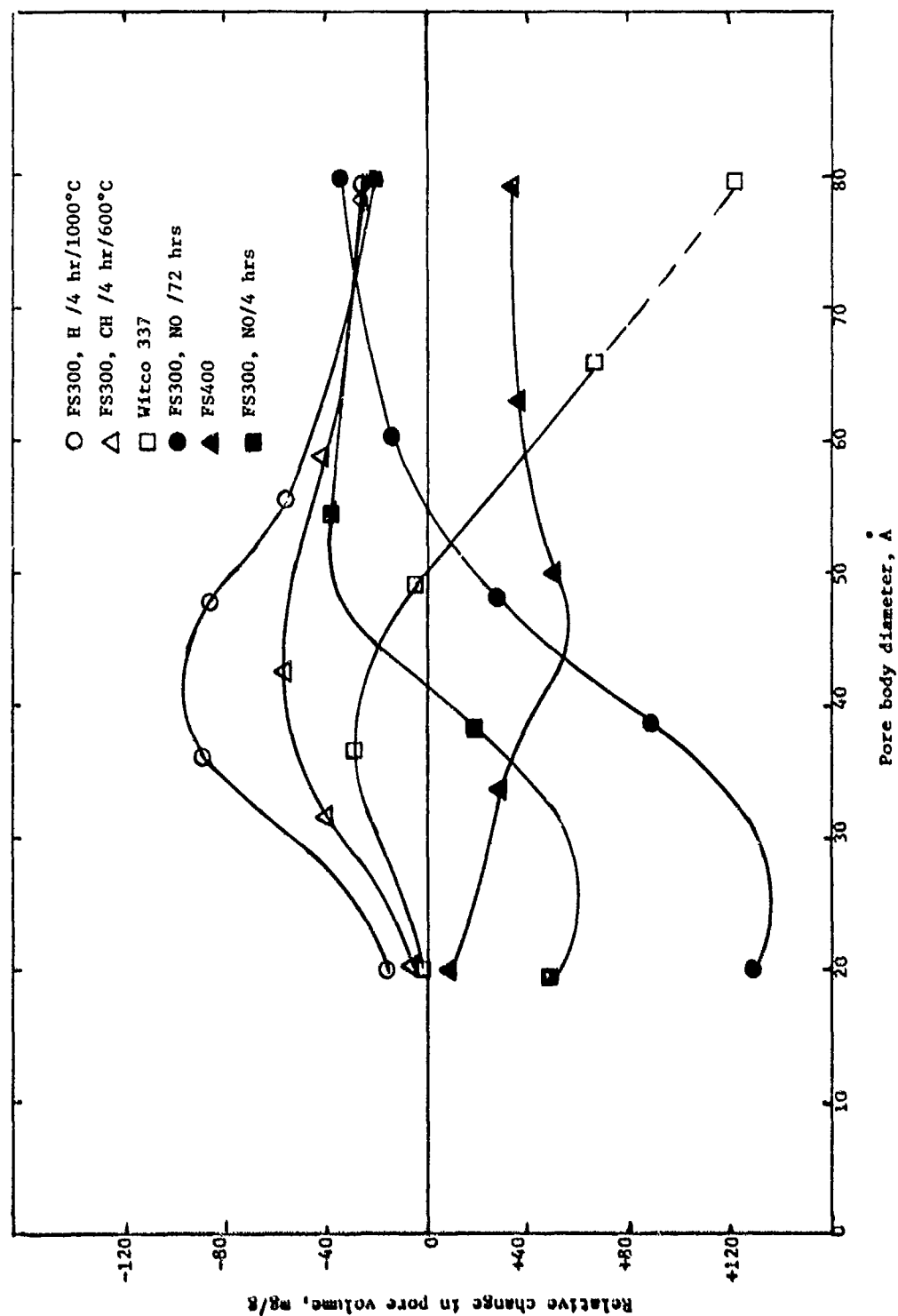
Figure 8. Change in body pore size distribution relative to 40/80 FS300.
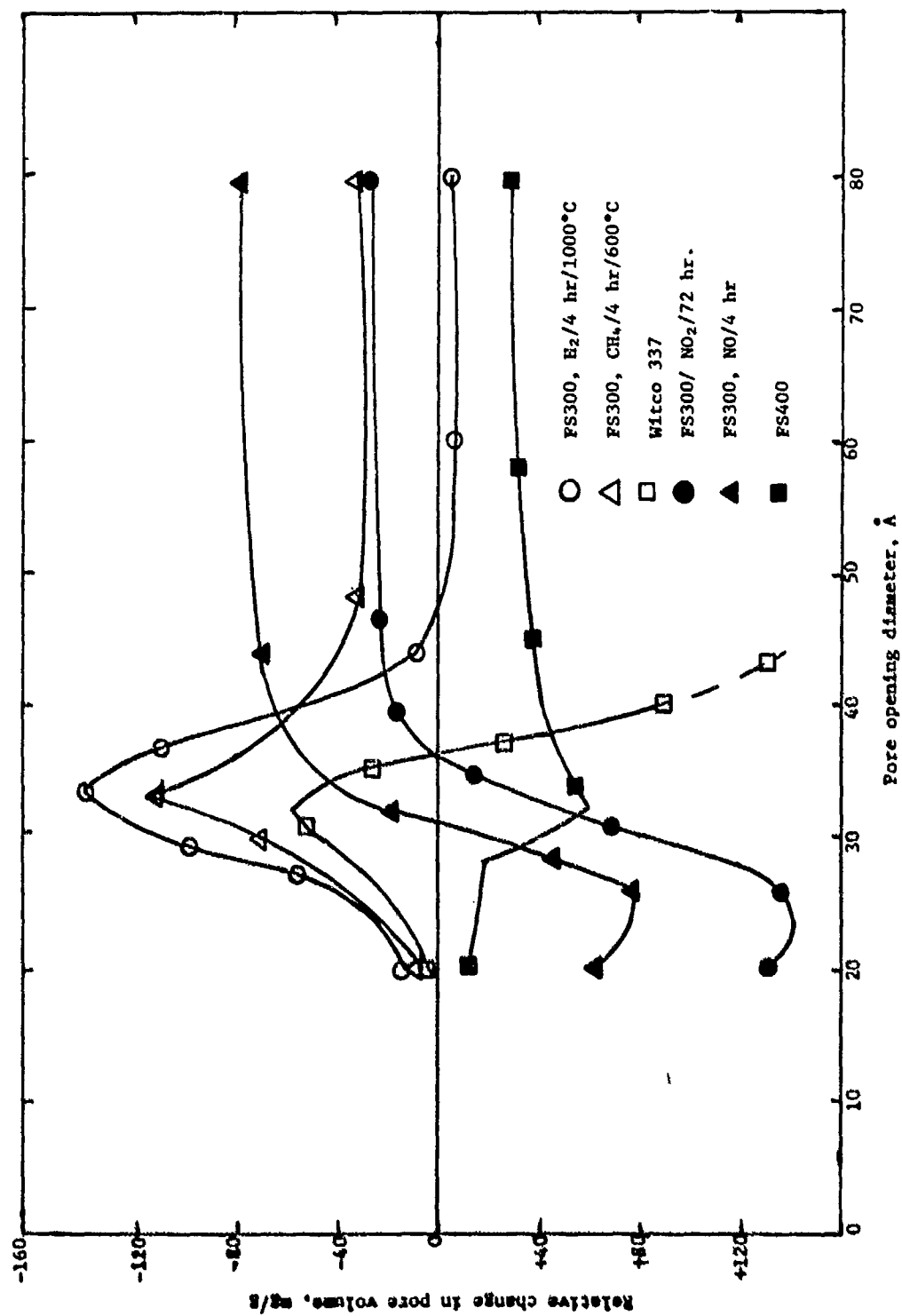
Figure 9. Change in opening pore size distribution relative to 40/80 FS300.

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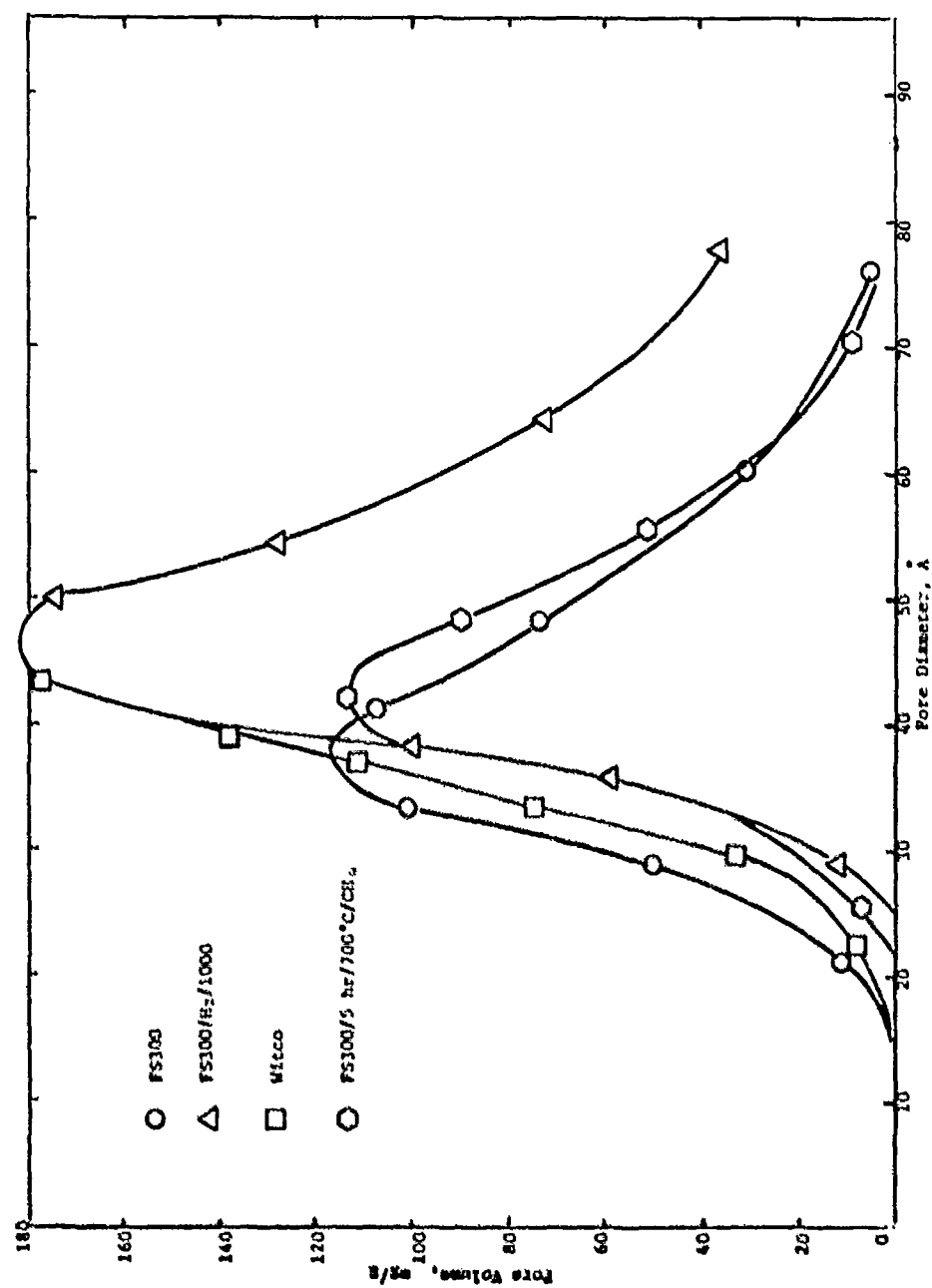
Figure 10. Pore size distribution of the pore openings relative to the pore bodies for FS300, FS300/H$_2$/1000°C, Witco 337, and FS300/CH$_4$/700°C/5 hr.

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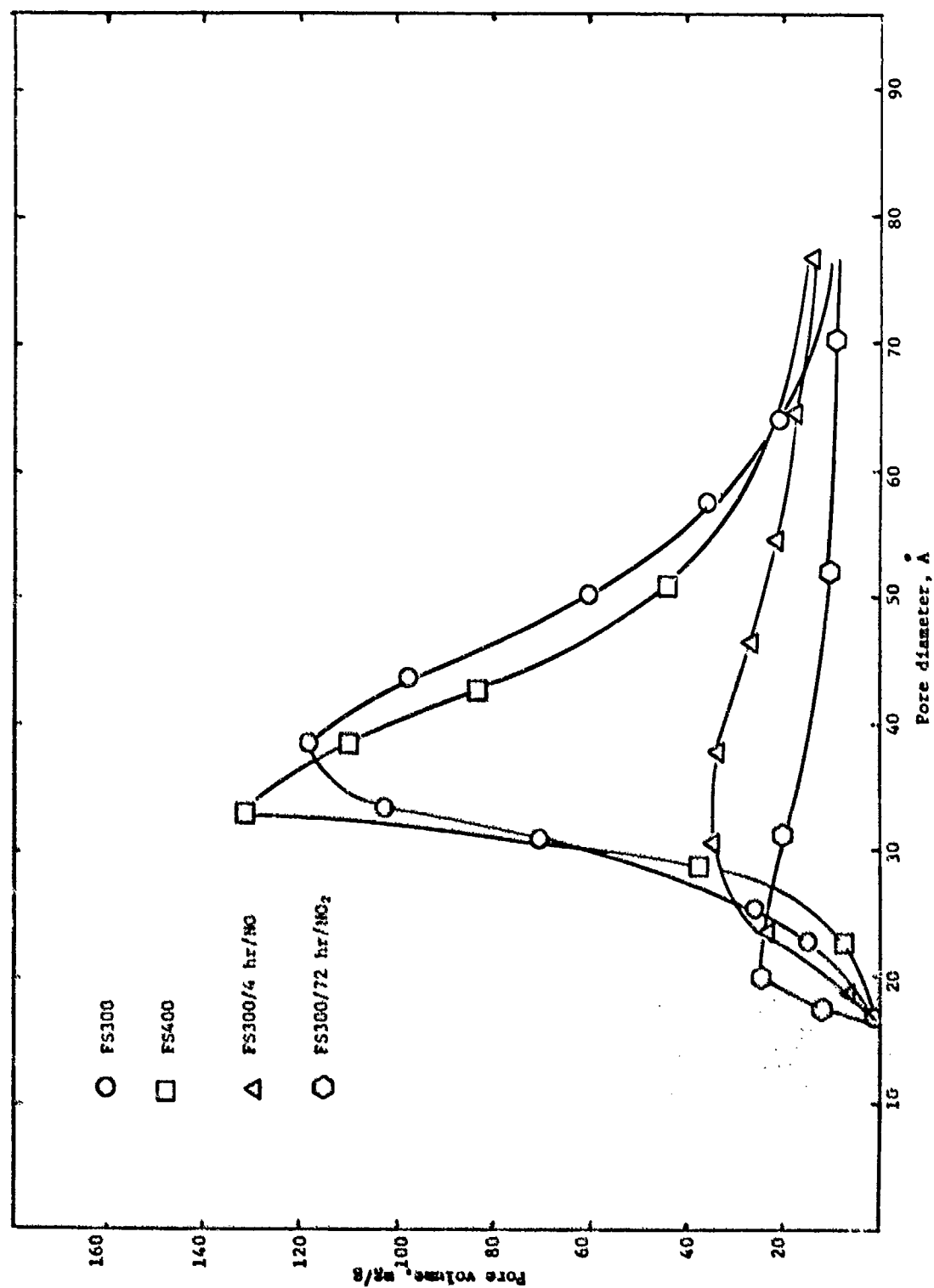
Figure 11. Pore size distribution of the pore openings relative to the pore bodies for FS300, FS400, FS300/4 hr/NO, and FS300/72 hr/NO$_2$.

APPENDIX
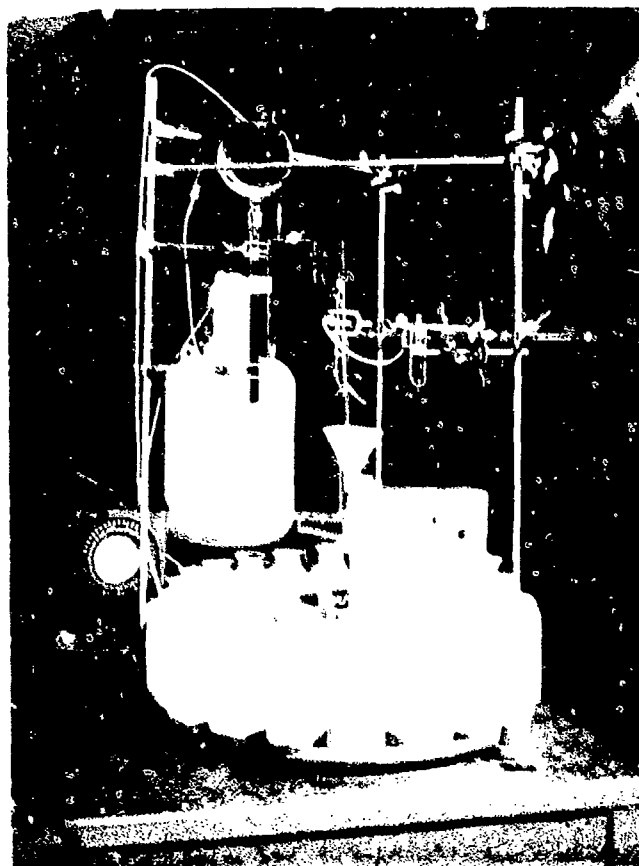
Figure A-1.   Automatic fraction collector with carbon column.

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Table A-1. Small column[a] adsorption/desorption cycling
as a function of particle size of FS300.

Volume[b]	Cumulative TNT			
	Retained, mg		Effluent, mg	
Thru liters	Coarse	40/80	Coarse	40/80
1st Adsorption				
1	116	118	1.70	0.0
2	227	236	5.90	0.0
3	342	354	1.30	0.02
4	444	472	13.90	0.20
5	542	590	18.40	0.0
6	632	704	24.90	0.0
7	719	818	28.30	0.0
8	796	932	38.40	0.0
1st Desorption				
0.1	474	674	57.9	72.3
0.2	591	805	72.1	86.5
0.3	617	831	75.4	89.0
0.4	626	837	76.4	89.0
0.5	636	847	78.3	91.0
1.0	644	853	79.0	91.7
2nd Adsorption				
1	120	120	1.1	1.1
2	240	241	0.0	0.0
3	360	362	2.4	0.18
4	478	484	3.0	0.08
5	596	604	3.9	0.70
6	668	729	52.7	0.00
7	757	854	35.8	0.00
8	841	979	41.6	0.50
2nd Desorption				
0.1	646	852	76.9	87.1
0.2	699	896	83.1	91.8
0.3	716	912	84.7	93.4
0.4	722	920	86.0	94.0
0.5	728	925	87.0	94.6
0.6	732	928	87.2	95.2
1.0	743	936	88.3	95.7

[a]Particle Size FS300	Weight, g	Length, cm	Diameter, cm	Volume, cm^3
Coarse	3.001	8.1	1.0	6.37
40/80	3.031	7.2	1.0	5.67

[b]Average rate 1.4 cm^3/min; adsorption from aqueous solution, desorption
with acetone.

Table A-1. Small column[a] adsorption/desorption cycling as a function of particle size of FS300 (Cont'd)

Volume[b]	Cumulative TNT			
	Retained, mg		Effluent, mg	
Thru liters	Coarse	40/80	Coarse	40/80
3rd Adsorption				
1	131	134	5.5	2.3
2	257	269	10.1	2.1
3	375	414	19.0	8.5
4	459	524	27.7	2.2
5	540	632	30.8	4.0
6	623	780	67.4	2.1
7	701	910	77.9	2.2
8	752	1039	80.0	2.1
3rd Desorption				
0.1	576	847	76.6	814
0.2	657	891	87.4	85.7
0.3	685	916	91.0	88.2
0.4	704	934	93.6	89.8
0.5	725	954	96.3	91.6
0.6	734	968	98.5	94.1
1.0	746	988	99.3	96.2
4th Adsorption				
1	132	137	8.0	3.3
2	267	274	5.1	2.9
3	323	383	56.4	2.9
4	409	480	25.9	15.0
5	501	618	63.0	17.5
6	600	743	56.0	31.0
4th Desorption				
0 1	444	516	73.7	69.5
0 2	584	659	97.4	89.0
0.3	606	681	100.5	91.8
0.4	616	691	102.5	93.0
0.5	626	701	104.5	95.0
1.0	651	721	107.0	97.1

[a]Particle size FS300	Weight, g	Length, cm	Diameter, cm	Volume, cm
Coarse	3.001	8.1	1.0	6.37
40/80	3.031	7.2	1.0	5.67

[b]Average rate 1.4 cm^3/min; adsorption from aqueous solution, desorption with acetone.

Table A-2. Small column[a] adsorption/desorption cycling as a function of particle size FS300.

| Volume[b] | Cumulative TNT | | | |
| | Retained, mg | | Effluent, mg | |
thru liters	Coarse	40/80	Coarse	40/80
1st Adsorption				
1	153	153	0.10	0.100
2	306	306	0.00	0.00
3	459	459	0.13	0.00
4	612	612	0.60	0.22
5	764	765	0.70	0.24
6	916	918	4.00	0.28
7	1065	1070	4.60	0.31
8	1206	1222	12.3	0.80
9	1339	1365	30.5	9.50
10	1445	1506	32.0	12.0
11	1540	1633	59.0	18.0
12	1622	1764	72.0	24.0
1st Desorption				
0.1	1049	1186	64.6	67.2
0.2	1232	1333	75.8	75.4
0.3	1272	1348	78.4	76.9
0.4	1385	1361	83.3	77.1
0.5	1496	1390	92.2	78.8
0.6	1507	1419	92.9	80.4
1.0	1517	1530	93.5	86.7
2nd Adsorption				
1	145	145	0.60	0.70
2	290	290	0.70	0.50
3	435	435	0.40	0.50
4	580	599	0.70	0.50
5	746	749	3.9	0.80
6	887	847	8.6	02.20
7	1160	1041	13.8	6.0
8	1225	1058	18.4	8.6

[a]Particle Size FS300	Weight, g	Length, cm	Diameter, cm	Volume, cm^3
Coarse	4.000	8.1	1.0	6.37
40/80	4.00	7.9	1.0	6.35

[b]Average rate 1.7 cm^3/min; adsorption from aqueous solution, desorption with acetone.

Table A-2. Small column[a] adsorption/desorption cycling as a function of particle size FS300. (cont'd)

Volume[b]	Cumulative TNT			
	Retained, mg		Effluent, mg	
thru liters	Coarse	40/80	Coarse	40/80
2nd Desorption				
0.1	959	814	78.2	69.0
0.2	994	863	81.1	73.2
0.3	1019	981	83.2	83.2
0.4	1045	997	85.3	84.6
0.5	1059	1010	85.4	85.7
1.0	1191	1038	97.2	88.0
3rd Adsorption				
1	110	120	0.10	0.20
2	225	240	0.33	0.60
3	330	360	0.30	0.30
4	480	480	0.35	0.30
5	649	600	1.06	0.40
6	806	767	12.6	22.8
7	1055	911	20.4	34.6
8	1189	1020	35.0	56.3
3rd Desorption				
0.1	772	620	64.9	60.8
0.2	955	932	80.4	81.6
0.3	963	962	81.0	84.6
0.4	979	979	82.4	86.2
0.5	994	991	83.6	87.4
1.0	1013	914	85.2	89.6

[a]Particle Size FS300	Weight,g	Length,cm	Diameter,cm	Volume, cm^3
Coarse	4.000	8.1	1.0	6.37
40/80	4.00	7.9	1.0	6.35

[b]Average rate 1.7 cm^3/min; adsorption from aqueous solution, desorption with acetone.

Table A-3. Small column[a] adsorption/desorption cycling
as a function of particle size FS300.

Volume[b]	Cumulative TNT			
	Retained, mg		Effluent, mg	
thru liters	Coarse	40/80	Coarse	40/80
1st Adsorption				
1	154	154	0.20	0.21
2	308	308	0.23	0.19
3	462	462	0.24	0.36
4	616	616	0.37	0.37
5	770	770	0.18	0.47
6	924	924	0.37	0.17
7	1078	1078	0.71	0.60
8	1232	1232	0.60	0.50
9	1386	1386	0.64	0.60
10	1540	1540	0.59	0.55
11	1694	1694	0.58	0.54
12	1848	1854	0.56	0.52
13	2002	2002	0.59	0.60
14	2156	2156	0.83	0.52
15	2300	2300	0.97	0.59
16	2454	2454	0.82	0.58
17	2608	2608	0.63	0.49
18	2761	2762	1.04	0.46
19	2913	2916	2.30	0.53
20	3064	3070	3.10	0.46
21	3205	3215	4.00	0.60
22	3344	3360	6.20	0.84
23	3481	3505	8.20	0.57
24	3625	3660	11.0	0.59
25	3761	3821	19.4	8.30
26	3891	3969	25.0	15.40
27	4017	4104	29.8	20.40
28	4136	4230	36.4	24.0
29	4245	4384	46.0	32.0

[a]Particle Size FS300	Weight,g	Length,cm	Diameter,cm	Volume, cm[3]
Coarse	10.000	21.2	1.0	16.6
40/80	10.00	21.9	1.0	17.2

[b]Average rate 4 cm^3/min; adsorption from aqueous solution, desorption
with acetone.

Table A-3. Small column[a] adsorption/desorption cycling
as a function of particle size FS300. (Cont'd)

	Cumulative TNT			
Volume[b]	Retained, mg		Effluent, mg	
thru liters	Coarse	40/80	Coarse	40/80
1st Desorption				
0.1	2640	3250	62.6	75.8
0.2	3431	3760	80.8	87.6
0.3	3585	3885	84.6	90.8
0.4	3602	3906	85.4	91.2
0.5	3610	3921	85.0	91.9
1.0	3670	3751	86.4	92.3
2nd Adsorption				
1	123	123	0.24	0.30
2	246	246	0.40	0.10
3	369	369	0.63	0.18
4	484	484	0.60	0.23
5	599	599	0.68	0.42
6	714	714	0.35	0.40
7	829	829	0.40	0.40
8	944	944	0.62	0.38
9	1060	1060	0.62	0.65
10	1176	1176	0.54	0.52
11	1292	1292	0.54	0.52
12	1408	1408	0.52	0.42
13	1524	1524	0.40	0.20
14	1643	1643	0.60	0.40
15	1762	1762	0.50	0.46
16	1871	1871	0.40	0.50
17	1990	1990	0.50	0.60
18	2109	2109	0.50	0.40
19	2228	2228	0.070	0.40
20	2347	2347	0.60	0.38
21	2466	2466	0.68	0.44
22	2585	2585	0.73	0.46
23	2700	2700	1.30	0.42
24	2808	2815	6.9	0.70
25	2912	2930	11.3	0.83

[a]Particle Size FS300	Weight,g	Length,cm	Diameter,cm	Volume, cm^3
Coarse	10.000	21.2	1.0	16.6
40/80	10.00	21.9	1.0	17.2

[b]Average rate 4 cm^3/min; adsorption from aqueous solution, desorption with acetone.

Table A-3. Small column[a] adsorption/desorption cycling
as a function of particle size FS300. (Cont'd)

Volume[b]	Cumulative TNT			
	Retained, mg		Effluent, mg	
thru liters	Coarse	40/80	Coarse	40/80
2nd Adsorption				
26	3013	3043	14.0	1.92
27	3108	3154	20.0	4.30
28	3199	3261	24.0	10.0
29	3286	3357	29.3	19.3
30	3365	3447	36.0	24.6
2nd Desorption				
0.1	2460	2630	73.1	75.7
0.2	2715	2968	80.8	85.4
0.3	2785	3015	82.8	87.8
0.4	2792	3029	83.1	88.0
0.5	2812	3043	83.6	88.2
1.0	2874	3106	85.4	89.4
3rd Adsorption				
1	125	125	0.10	0.00
2	250	250	0.10	0.00
3	375	375	0.09	0.08
4	500	500	0.50	0.33
5	636	636	0.10	0.30
6	772	772	0.70	0.49
7	907	908	0.91	0.55
8	1043	1044	0.60	0.48
9	1155	1155	0.54	0.65
10	1267	1268	0.70	0.40
11	1379	1380	0.70	0.60
12	1527	1529	1.23	0.31
13	1657	1660	1.70	0.18
14	1787	1792	2.30	0.95
15	1927	1936	3.10	0.30
16	2064	2074	3.00	1.50
17	2201	2212	3.48	2.38
18	2311	2324	7.50	8.10
19	2421	2428	12.00	16.00
20	2525	2503	15.00	34.00
21	2623	2580	21.0	52.0

[a]Particle Size FS300	Weight,g	Length,cm	Diameter,cm	Volume, cm^3
Coarse	10.000	21.2	1.0	16.6
40/80	10.00	21.9	1.0	17.2

[b]Average rate 4 cm^3/min; adsorption from aqueous solution, desorption
with acetone.

Table A-3. Small column[a] adsorption/desorption cycling
as a function of particle size FS300. (cont'd)

	Cumulative TNT			
Volume[b]	Retained, mg		Effluent, mg	
thru liters	Coarse	40/80	Coarse	40/80
3rd Desorption				
0.1	1065	1520	40.0	57.6
0.2	1773	2038	66.6	78.2
0.3	2194	2479	82.4	95.2
0.4	2243	2532	84.9	97.0
0.5	2265	2550	84.6	98.0
0.6	2277	2562	85.8	98.3
1.0	2295	2581	86.2	99.2

[a]Particle Size FS300	Weight,g	Length,cm	Diameter,cm	Volume, cm^3
Coarse	10.000	21.2	1.0	16.6
40/80	10.00	21.9	1.0	17.2

[b]Average rate 4 cm^3/min; adsorption from aqueous solution, desorption
with acetone.

Table A-4. Small column[a] adsorption/desorption cycling
as a function of particle size FS300.

Volume[b]	Cumulative TNT			
	Retained, mg		Effluent, mg	
thru liters	Coarse	40/80	Coarse	40/80
Adsorption				
1	154	154	0.31	0.24
2	308	308	0.51	0.60
3	462	462	0.46	0.31
4	616	616	0.34	0.34
5	770	770	0.75	0.80
6	924	924	0.61	0.71
7	1078	1078	0.63	0.71
8	1232	1232	0.84	0.71
9	1386	1386	0.49	0.37
10	1540	1540	0.55	0.39
11	1694	1694	0.73	0.68
12	1848	1848	0.81	0.70
13	2002	2002	0.64	0.34
14	2156	2156	0.70	0.42
15	2310	2310	0.62	0.74
16	2464	2464	0.79	0.82
17	2618	2618	0.70	0.72
18	2872	2872	0.79	0.72
19	3040	3040	0.57	0.60
20	3208	3208	0.30	0.35
21	3376	3376	0.29	0.63
22	3544	3544	0.11	0.27
23	3542	3542	0.11	0.17
24	3722	3722	0.24	0.29
25	3872	3872	0.61	0.21
26	4022	4022	0.23	0.60
27	4172	4172	0.32	0.65
28	4327	4327	0.36	0.10
29	4482	4482	0.10	0.40
30	4627	4627	0.36	0.21
31	4772	4772	0.21	0.34
32	4917	4917	0.12	0.32

[a]Particle Size FS300	Weight,g	Length,cm	Diameter,cm	Volume, cm^3
Coarse	20.00	12.3	2.0	39.4
40/80	20.00	12.3	2.0	39.4

[b]Average rate 4 cm^3/min; adsorption from aqueous solution, desorption
with acetone.

Table A-4. Small column[a] adsorption/desorption cycling
as a function of particle size FS300. (Cont'd)

| Volume[b] | Cumulative TNT | | | |
| | Retained, mg | | Effluent, mg | |
thru liters	Coarse	40/80	Coarse	40/80
Adsorption (cont'd)				
33	5062	5062	0.18	0.43
34	5205	5205	0.24	0.63
35	5348	5348	0.59	0.36
36	5491	5491	0.56	0.03
37	5634	5634	0.56	0.50
38	5776	5777	1.3	0.60
39	5917	5921	2.8	0.68
40	6055	6065	5.0	0.54
41	6190	6208	7.7	0.51
42	6325	6351	8.1	0.41
43	6461	6494	9.6	0.70
44	6604	6647	12.0	2.4
45	6745	6798	14.6	4.9
46	6880	6847	20.0	6.0
47	7011	6995	24.5	10.0
48	7125	7107	30.0	12.5
49	7242	7211	38.0	18.0
50	7354	7308	43.0	29.0
Desorption				
0.1	3380	3870	46.0	52.4
0.2	5460	5775	74.0	78.3
0.3	5900	6330	80.1	85.7
0.4	6079	6511	82.5	88.4
0.5	6169	6584	85.3	89.2
1.0	6349	6786	86.4	92.2

[a]Particle Size FS300	Weight,g	Length,cm	Diameter,cm	Volume, cm[3]
Coarse	20.00	12.3	2.0	39.4
40/80	20.00	12.3	2.0	39.4

[b]Average rate 4 cm[3]/min; adsorption from aqueous solution, desorption
with acetone.

Table A-5. Batch adsorption/desorption cycling of
pretreated FS300 carbons *

Carbon treatment	Cycle	Specific adsorption	Specific desorption	Retained	Cumulative retained
Virgin	1	0.45	0.33	0.12	0.12
	2	0.43	0.32	0.11	0.23
	3	0.42	0.31	0.11	0.34
	4	0.39	0.30	0.09	0.43
	5	0.39	0.32	0.07	0.50
	6	0.34	0.28	0.06	0.56
TNT-sat/	1	0.34	0.31	0.03	0.03
sohx	2	0.34	0.28	0.06	0.09
extracted	3	0.32	0.26	0.06	0.15
	4	0.32	0.25	0.07	0.22
	5	0.27	0.22	0.05	0.27
	6	0.22	0.16	0.06	0.33
CH_4/600°C/	1	.38	.25	.13	.13
4 hr	2	.31	0.25	.06	.19
	3	.34	.28	.06	.25
	4	.35	.26	.09	.34
	5	.31	.24	.07	.41
	6	.32	.26	.06	.47

* All carbons are 40/80 mesh FS300 unless otherwise specified.

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Table A-5. Batch adsorption/desorption cycling of pretreated FS300 carbons *(Cont'd)

Carbon treatment	Cycle	Specific adsorption	Specific desorption	Retained	Cumulative retained
CH$_4$/650°C/ 4 hr	1	.43	.30	.13	.13
	2	.38	.26	.12	.25
	3	.34	.32	.02	.27
	4	.35	.32	.03	.30
	5	.32	.30	.02	.32
	6	.30	.23	.07	.39
CH$_4$/700°C 3 hr	1	0.42	0.31	0.10	0.10
	2	0.42	0.34	0.08	0.18
	3	0.42	0.33	0.09	0.27
	4	0.38	0.28	0.10	0.37
	5	0.37	0.28	0.09	0.46
	6	0.37	0.30	0.07	0.53
CH$_4$/700°C 5 hr	1	0.39	0.26	0.13	0.13
	2	0.42	0.32	0.10	0.23
	3	0.40	0.33	0.07	0.30
	4	0.37	0.27	0.10	0.40
	5	0.36	0.28	0.08	0.48
	6	0.32	0.27	0.05	0.53

*All carbons are 40/80 mesh FS300 unless otherwise specified.

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Table A-5. Batch adsorption/desorption cycling of pretreated FS300 carbons *(Cont'd)

Carbon treatment	Cycle	Specific adsorption	Specific desorption	Retained	Cumulative retained
CH$_4$/750°C 4 hr	1	0.30	0.22	0.08	0.08
	2	0.25	0.24	0.01	0.09
	3	0.26	0.24	0.02	0.11
	4	0.26	0.20	0.06	0.19
	5	0.25	0.20	0.05	0.22
	6	0.25	0.19	0.06	0.28
Ar/1000°C 4 hr	1	0.41	0.31	0.10	0.10
	2	0.42	0.34	0.08	0.18
	3	0.34	0.34	0.00	0.18
	4	0.36	0.25	0.11	0.29
	5	0.34	0.20	0.14	0.43
	6	0.32	0.23	0.09	0.52
H$_2$/1000°C/ 40/80 4 hr	1	0.48	0.22	0.26	0.26
	2	0.45	0.38	0.07	0.33
	3	0.42	0.37	0.05	0.38
	4	0.42	0.36	0.06	0.44
	5	0.40	0.35	0.05	0.49
	6	0.35	0.31	0.04	0.53
NO$_2$/72 hr water washed	1	0.33	0.27	0.06	0.06
	2	0.34	0.25	0.09	0.15
	3	0.28	0.23	0.05	0.20
	4	0.28	0.22	0.06	0.26
	5	0.28	0.23	0.05	0.31
	6	0.27	0.22	0.05	0.36

*All carbons are 40/80 mesh FS300 unless otherwise specified.

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Table A-5. Batch adsorption/desorption cycling of pretreated FS300 carbons* (Cont'd)

Carbon treatment	Cycle	Specific adsorption	Specific desorption	Retained	Cumulative retained
NO_2/72 hr freon washed (air dried)	1	0.32	0.26	0.06	0.06
	2	0.30	0.26	0.04	0.10
	3	0.28	0.26	0.02	0.12
	4	0.28	0.26	0.02	0.14
	5	0.28	0.22	0.06	0.20
	6	0.26	0.23	0.03	0.27
NO_2/72 hr	1	0.34	0.24	0.10	0.10
	2	0.32	0.27	0.05	0.15
	3	0.32	0.26	0.06	0.21
	4	0.32	0.25	0.07	0.28
	5	0.31	0.26	0.05	0.33
	6	0.31	0.24	0.07	0.40
NO_2/72 hr freon/ acetone wash	1	0.28	0.21	0.07	0.07
	2	0.25	0.22	0.03	0.11
	3	0.24	0.21	0.03	0.14
	4	0.25	0.20	0.05	0.19
	5	0.25	0.19	0.04	0.23
	6	0.20	0.16	0.04	0.27

*All carbons are 40/80 mesh FS300 unless otherwise specified.

Table A-5. Batch adsorption/desorption cycling of
pretreated FS300 carbons *(Cont'd)

Carbon treatment	Cycle	Specific adsorption	Specific desorption	Retained	Cumulative retained
NO₂/18 hr / RT	1	0.29	0.23	0.06	0.06
	2	0.30	0.23	0.07	0.13
	3	0.30	0.25	0.05	0.18
	4	0.29	0.24	0.05	0.23
	5	0.29	0.23	0.06	0.29
	6	0.24	0.24	0.00	0.29
NO₂, 4 hr	1	0.32	0.23	0.09	0.09
	2	0.32	0.23	0.09	0.18
	3	0.29	0.22	0.07	0.25
	4	0.28	0.22	0.06	0.31
	5	0.25	0.22	0.03	0.34
	6	0.25	0.20	0.05	0.39
NO₂/Freon 4 hr	1	0.29	0.24	0.05	0.05
	2	0.30	0.27	0.03	0.08
	3	0.30	0.25	0.05	0.13
	4	0.29	0.26	0.03	0.16
	5	0.25	0.25	0.00	0.16
	6	0.25	0.24	0.01	0.17
NO/RT/72 hr	1	0.37	0.27	0.10	0.10
	2	0.35	0.26	0.09	0.19
	3	0.29	0.25	0.04	0.23
	4	0.30	0.25	0.05	0.28
	5	0.30	0.25	0.05	0.33
	6	0.28	0.23	0.05	0.38

*All carbons are 40/80 mesh FS300 unless otherwise specified.

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Table A-5. Batch adsorption/desorption cycling of
pretreated FS300 carbons *(Cont'd)

Carbon treatment	Cycle	Specific adsorption	Specific desorption	Retained	Cumulative retained
NO/4 hr freon washed	1	0.39	0.25	0.14	0.14
	2	0.32	0.29	0.03	0.17
	3	0.32	0.28	0.04	0.21
	4	0.30	0.27	0.03	0.24
	5	0.28	0.27	0.01	0.25
	6	0.27	0.22	0.05	0.29
NO/4 hr/ H_2O	1	0.44	0.30	0.14	0.14
	2	0.42	0.31	0.11	0.25
	3	0.39	0.32	0.07	0.32
	4	0.40	0.34	0.06	0.38
	5	0.40	0.30	0.10	0.48
	6	0.38	0.31	0.07	0.55
NO/4 hr freon/acetone	1	0.34	0.22	0.12	0.12
	2	0.30	0.24	0.06	0.18
	3	0.28	0.24	0.04	0.22
	4	0.30	0.21	0.09	0.31
	5	0.30	0.20	0.10	0.41
	6	0.28	0.22	0.06	0.47

*All carbons are 40/80 mesh FS300 unless otherwise specified.

Table A-6. Column adsorption/desorption cycling of pretreated carbons.

Treatment	Cycle	Sp. Ads. at 1 ppm breakthrough	Specific adsorption	Specific desorption	Retained	Cumulative retained
Virgin	1	0.48	0.53	0.39	0.14	0.14
	2	0.39	0.42	0.36	0.06	0.20
	3	0.36	0.39	0.32	0.07	0.27
	4	0.34	0.38	0.34	0.04	0.31
	5	0.32	0.38	0.30	0.08	0.39
	6	0.29	0.34	0.33	0.01	0.40
	7	0.30	0.36	0.33	0.03	0.43
CH$_4$/700°C 4 hr	1	0.42	0.42	0.28	0.14	0.14
	2	0.39	0.43	0.32	0.11	0.25
	3	0.28	0.33	0.27	0.06	0.31
	4	0.27	0.35	0.29	0.06	0.31
	5	0.29	0.34	0.28	0.06	0.43
	6	0.25	0.33	0.29	0.04	0.47
	7	0.21	0.26	0.21	0.05	0.52
H$_2$/1000°C 4 hr	1	0.58	0.62	0.52	0.10	0.10
	2	0.46	0.52	0.41	0.11	0.21
	3	0.46	0.50	0.40	0.10	0.31
	4	0.40	0.47	0.36	0.11	0.42
	5	0.35	0.39	0.29	0.10	0.52
	6	0.30	0.36	0.27	0.09	0.61
	7	0.26	0.33	0.27	0.06	0.67

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Table A-6. (Cont'd)

Treatment	Cycle	Sp. Ads. at 1 ppm breakthrough	Total specific adsorption	Specific desorption	Retained	Cumulative retained
NO$_2$/72 hr	1	0.35	0.39	0.27	0.12	0.12
	2	0.22	0.24	0.20	0.04	0.16
	3	0.21	0.29	0.25	0.04	0.20
	4	0.20	0.28	0.24	0.04	0.24
	5	0.20	0.30	0.24	0.06	0.30
	6	0.17	0.26	0.18	0.08	0.38
	7	0.16	0.27	0.21	0.06	0.44
NO/4 hr	1	0.44	0.51	0.42	0.09	0.09
	2	0.35	0.45	0.43	0.02	0.11
	3	0.27	0.35	0.28	0.07	0.18
	4	0.22	0.31	0.25	0.06	0.24
	5	0.25	0.32	0.20	0.12	0.36
	6	0.24	0.26	0.19	0.07	0.43
	7	0.24	0.16	0.20	0.06	0.49
Witco	1	0.58	0.59	0.44	0.15	0.15
	2	0.54	0.60	0.46	0.14	0.29
	3	0.45	0.55	0.46	0.09	0.38
	4	0.43	0.49	0.43	0.06	0.44
	5	0.38	0.39	0.39	0.00	0.44
	6	0.38	0.46	0.42	0.04	0.48
	7	0.36	0.36	0.33	0.03	0.52

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Table A6. Cont'd

Treatment	Cycle	Sp. Ads. at 1 ppm breakthrough	Specific adsorption	Specific desorption	Retained	Cumulative retained
FS400	1	0.61	0.63	0.39	0.24	0.24
	2	0.42	0.46	0.40	0.06	0.30
	3	0.41	0.45	0.44	0.01	0.31
	4	0.33	0.37	0.32	0.05	0.36
	5	0.32	0.36	0.33	0.03	0.39
	6	0.33	0.41	0.38	0.03	0.42
	7	0.32	0.34	0.31	0.03	0.45

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